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BOREHOLE SEALING LITERATURE REVIEW OF PERFORMANCE REQUIREMENTS AND MATERIALS

Report No. 84-380-K

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ABSTRACT

To ensure the safe disposal of nuclear wastes, all potential pathways for radionuclide release to the biosphere must be effectively sealed. This report presents a summary of the literature up to August 1982 and outlines the placement, mechanical property and durability-stability requirements for borehole sealing. An outline of the materials that have been considered for possible use in borehole sealing is also included.

Cement grouts are recommended for further study since it is indicated in the literature that cement grouts offer the best opportunity of effectively sealing boreholes employing present technology. However, new and less well known materials should also be researched to ensure that the best possible borehole plugging system is developed.

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BOREHOLE SEALING LITERATURE REVIEW OF PERFORMANCE REQUIREMENTS AND MATERIALS

1.0 INTRODUCTION

The Canadian reference concept for high-level radioactive waste disposal is to build a mined repository of approximately 1 km depth in a granitic pluton at an as yet undetermined location in the Canadian Shield. To ensure isolation of these nuclear wastes, all boreholes in the vicinity of a disposal site will require sealing. In this report, the literature available up to August 1982 (D. Piccinin's term of work) on borehole sealing research has been reviewed to determine the candidate materials and performance requirements of borehole sealants. Since then, many more references relating to borehole sealing have been acquired and/or become available. While these newer references are not included in this review, they are listed to at least provide sources for further information (references 56 to 78). Even though the review is somewhat outdated, the performance parameters outlined are still valid.

2.0 PERFORMANCE REQUIREMENTS

To seal a borehole located at a nuclear waste repository site, many requirements have been presented in the literature. The performance requirements are outlined in this section and listed in Table I. Included are the requirements for placement, mechanical properties, and long-term stability and durability.

2.1 Placement Requirements

To ensure proper placement, the seal material should have the following properties.

2.1.1 Working Time

The working time must be of sufficient length to ensure that setting does not occur during transportation and placement/1/. Soon after placement, the material should set in order to reduce the possibility of contamination from materials adhering to the borehole surfaces/2/. A 2 to 3 hour working time was the

objective for work completed at the U.S. Army Engineer Waterways Experiment Station (WES)/3/. Methods used for measuring the working time include an automatic testing procedure similar to the Method of Test for Time of Setting of Grout Mixtures (CRD-C82-76)/3/, a penetrometer method (ASTM C403-70)/4/ and Vicat needles/5,6/.

2.1.2 Bleeding and Segregation

Bleeding and segregation must be minimized/7/ to reduce strength differences that can occur with a plug mass and to reduce the formation of weaker planes. The initial bleeding rate and the bleeding capacity of the grout have been used to measure this property (ASTM C243-65)/4/.

No bleeding limits are suggested in the literature, but at Oak Ridge National Laboratory (ORNL), no bleeding was observed for a saltcrete-fly ash mix with a bleeding rate of less than 7×10^{-7} cm^3 H_2O/cm^2 sec and a bleeding capacity of less than 1×10^{-4} cm^3 H_2O/cm^3/4/. Therefore, grouts having lower bleeding rates using this test method would likely satisfy this requirement of minimal bleeding. Bleeding limits should be studied; however, since higher values may be also found to produce acceptable bleeding characteristics.

2.1.3 Fluidity

A material of fluid consistency is required to permit transportation and placement of the material/7/. Both the flow cone and the K-slump tester have been used to obtain a measure of fluidity. ORNL discontinued the use of the K-slump tester since it was found to be an inaccurate method of measurement/4/. Use of the K-slump tester by Ontario Hydro for fluidity testing of concrete has also been unsuccessful/8/.

The criteria for pumpability for the Bell Canyon test was a flow cone value of 18 seconds or less at the end of 3 hours. Grouts with higher flow times were withdrawn from further study/9/. This flow may prove to be adequate for other sites but factors such as the depth of the borehole, the grouting equipment and the transport time must be considered individually.

2.1.4 Pumpability

The sealant must be pumpable in order to transport materials to the expected borehole sealing depths of 1 km/1/. The flow cone was also employed at the Waterways Experiment Station, where a flow time of 12.8 seconds was described as being in a suitable range for flowability, pumpability and to produce a self-consolidating grout/6/.

2.1.5 Sealing of Fissures

The sealant must be able to seal fissures surrounding the boreholes/4/. This may limit the maximum allowable particle size to permit the sealing of small fissures since the preferred ratio of crack width to maximum grain size is at least 3.0 to 1.0/10/. It is indicated in the literature that cracks as small as 0.1 mm width will require sealing in order to sufficiently reduce the perme-

ability of the host rock/11/. This indicates that a maximum grain size of less than 33 microns is required. This may result in separate materials being used to seal the fissures and to plug the borehole or a very fine grained material, possibly a CSA Type 30 cement, used for both purposes. For a Type 30 cement, less than 0.2% is retained on the 90 micron sieve and 8% on the 45 micron sieve; in comparison for a Type 10 cement, 4% is retained on the 90 micron sieve and 15% on the 45 micron/12/.

2.2 Mechanical Properties

A wide range of mechanical properties is required for borehole sealants. Many of these properties should have values similar to those of the host rock to create a compatible and stable system.

2.2.1 Permeability

The sealant, the plug-rock interface and the rock in the vicinity of the borehole must have low permeability to both liquids and gases/3/. To achieve a sufficiently dense medium, it is estimated that the permeability should be from 10^{-12} to 10^{-13} m/s/11/. This will require sealing of 0.1 mm fissures to reduce the crack width to 10^{-3} mm/11/. The sealant should have a similar permeability including the plug-rock interface which is the most critical area. At ORNL a grout with a permeability of approximately 2.2×10^{-11} m/s was developed. This grout, consisting of ASTM Type I cement, bituminous fly ash, sand and water, was used to plug a simulated borehole in Westerly granite/13/. A permeability of 1.2×10^{-11} m/s was achieved with a grout (ASTM Type V cement, natural pozzolan, sand, water reducing agent, aluminum powder) in basalt at the Rockwell Laboratories/5/. These values reported in the literature suggest that materials with sufficiently low permeabilities can be developed. The sealing of fissures to reduce the permeability of the host rock may be difficult.

The sealing of fissures to reduce the permeability of the host rock can be accomplished in the vicinity of the borehole, but the permeability cannot be reduced for the entire rock mass. This has led others/2,7/ to conclude that the permeability of the plug need only be equal to that of the host rock. The permeability of granite has been reported to range from 10^{-7} to 10^{-11} m/s at depths of 425 m at Atikokan, Ontario, by D'Appolonia Consulting Engineers and 10^{-7} to 10^{-9} m/s at 1800 m by Los Alamos Scientific Laboratory at the Fenton Hill geothermal site/14/. The matrix permeability of granite may be as low as 10^{-15} m/s/14/.

The requirement for maintaining the low permeabilities over a long time period results in many other performance requirements coming into play since the permeability can be affected by the environment, including leaching, radioactive exposure and thermal effects. The permeability is the most important property of the borehole sealant.

2.2.2 Porosity

Generally, in achieving a low porosity, a low permeability is obtained and the effects of weathering are reduced/1,15/. Research has shown that the actual

pore sizes are more critical to permeability than the total pore volume. Large pores, arbitrarily defined as pores of greater than 0.132 μm diameter by Mehta and Manmohan, have a greater effect on permeability than small pores/16/. Therefore, the development of materials with low porosity and fine pore size distributions will produce sealants with low permeabilities.

Porosity has been measured by determining the difference between the saturation density and the dry density/3,4,17/, by the buoyancy method (API RP-40 (1960))/5/, and the Washburn-Bunting Method (air is extracted from the pore space and measured directly)/18/. Pore size analysis data have been obtained with the use of a mercury intrusion apparatus/16/.

The porosity of grouts for use in borehole sealing has been studied. For example, a porosity of 33% was obtained for a grout placed in basalt/5/, but pore size distribution was not measured.

2.2.3 Density

The requirement to design a dense plug material/1,19/ is related to the permeability and porosity requirements. Density has been measured by determining a surface dry weight in air and an immersed weight/6/. This density is called the apparent density since interior pores are not compensated for. The solid volume density is higher since it compensates for the volume occupied by interconnected pores and can be obtained using a helium air comparison pycnometer/20/.

The densities of neat cement pastes generally range from 2200 to 2300 kg/m^3/21/. A grout tested at ORNL, incorporating ASTM Type I cement, sand, salt, fly ash and water, resulted in a density of 2000 kg/m^3/4/. The density of granite is higher than this at 2650 kg/m^3/22/. It is not anticipated that density compatibility is required, but this could be obtained through use of higher density aggregates.

2.2.4 Strength

Sufficient strength is required to withstand stresses including those induced by temperature, squeezing, over-burden and uplift pressures. It has been mentioned by Gulick/23/ that adequate strength of greater than 24 MPa will be obtained automatically for cement grouts designed for low permeability due to their lower water-cement ratio. A scan through the literature confirmed that grouts designed for low permeability have strengths well in excess of 24 MPa when 50 mm grout cubes (ASTM C109) are tested in compression. Strengths lower than this limit were obtained at 7 days, but by 91 days, strengths in excess of 45 MPa are obtained for ASTM Type I cement, fly ash and water mixes/4/. The compressive strength of granite averages about 130 MPa for the rock mass/22/. If the 24 MPa strength is sufficient, actual design of grouts to achieve higher strengths is not required since grouts designed for low permeabilities will easily achieve the strength requirements. However, if higher strengths are required, compressive strengths of over 200 MPa have been achieved for concretes containing silica fume and superplasticizers/24/. These high strength materials would likely offer improvement to other properties such as permeability.

2.2.5 Bond Strength

A good bond between the host rock and the borehole plug will reduce the permeability and the probability of separation along this interface/2,3,19/. The bond strength has been evaluated by determining the force required to extrude a plug from the host rock and dividing this force by the contact area between the plug and rock/5/. Since the strength depends on the contact area, an acceptable limit for the bond strength will depend on the length of the seal/2/. It is thought that plugs designed for 3.5 MPa hydraulic pressure are suitable for borehole sealing and are readily achieved for all but very short lengths of seal/2/.

No test results have been reported on bond strengths with granite. In basalt, a strength of 10 MPa was obtained for clean rock and 2.5 MPa for mud-contaminated rock/5/. In anhydrite, a strength of almost 5 MPa was achieved at 7 days and increased to 14 MPa at 28 days/9/. Therefore, it appears there should be little difficulty in obtaining 3.5 MPa bond strength for other host rocks providing that the borehole walls are clean.

2.2.6 Expansion

A method to improve the bond between the plug and host rock is to employ a material capable of expansion/1/. In some cases, it is stated that a material with controlled expansive properties is required/3/. The expansion should preferably occur after setting and should be sufficient to produce a good bond and yet not so high as to induce undesirable stresses.

Unrestrained expansion prisms/3/, restrained expansion prisms (ASTM C806-75)/9/ and test methods for expansion of grout mixtures/5/ have been used to measure the expansion. The literature does not indicate the optimum expansion, but it should be noted that at Rockwell Laboratories, the optimum content of the expansive additive selected produced 8% expansion prior to setting/5/.

2.2.7 Homogeneity

The effects of varying responses to an environmental condition can be reduced by employing a homogeneous plug material/1/. A non-homogeneous material could have, for example, a coefficient of thermal expansion that varies through the material and extreme temperature changes could cause differential stress build-up, possibly resulting in cracking. Bleeding and segregation, discussed previously, would be the most likely causes of heterogeneity.

2.2.8 Moisture and Thermally Induced Shrinkage

Shrinkage should be minimized to ensure that cracking does not result and separation between the plug material and host rock does not occur. For a grout studied at Rockwell Laboratories, less than 0.1% shrinkage resulted when tested for early volume change (ASTM C-827 (1977))/5/. Another grout composed of ASTM Type I cement, fly ash, sand, salt and water also gave less than 0.1% linear shrinkage at 180 days/4/. Under the borehole conditions, it is possible that no

shrinkage will result since drying would be restricted. As mentioned previously, an expansive additive can be used to counteract shrinkage tendencies.

2.2.9 Deformability

Sufficient deformability will allow for rock movement without the development of cracks. It is expected that cement grouts can withstand the stresses created by rock movement since the stresses will be relieved through creep, and also the strength of cement grouts in triaxial compression should be sufficient. If additional deformability is necessary, polymers can be incorporated in the grout, for example, adding styrene butadiene to cements produced larger deflections with load/25/. Deformability, at least as much as granite, will be an important property if seismic activity is expected in the vicinity of the nuclear waste repository site.

2.2.10 Thermal Properties

A coefficient of thermal expansion similar to that of the host rock will reduce differential responses to temperature and thereby reduce any potential for cracking/2,19/. The coefficient of thermal expansion for granite is $8.1 \pm 2.7 \times 10^{-6}$ m/m/°C/22/. Values for hydrated portland cement pastes range between 11×10^{-6} and 16×10^{-6} m/m/°C, but values as high as 20.7×10^{-6} m/m/°C have been obtained depending on the degree of saturation/24/. Sanded grouts will have lower thermal expansions in the order of 5×10^{-6} m/m/°C/26/.

A second thermal property, thermal conductivity, should also be considered. The thermal conductivity of granite is about 2.9 W/m/°C/22/. Thermal conductivities were found to be 0.6 W/m/°C for cement, fly ash, water mixes; 0.65 to 1.76 W/m/°C for cement, sand, water mixes; and between 1.24 and 1.53 W/m/°C for cement, sand, salt and fly ash, water mixes studied at ORNL/4/. Values of thermal conductivity were required to determine thermal distributions and thermally induced stresses developed in cementitious materials/4/.

The heat of hydration of cement grouts should also be considered since thermal shrinkage cracking can result on cooling. The other thermal properties are important at later ages, especially if large variations in temperature are expected to occur at the plug location.

2.2.11 Elastic and Plastic Properties

The sealant and the host rock should have similar elastic and plastic properties to produce a compatible system/2,22/. The sealant should have a lower value of Young's Modulus than the surrounding rock since earlier failures occur for materials with the values higher than the host rock/2/. This results since the higher Modulus materials attract higher loadings. Values of static Young's Modulus for granite range from 16 to 83 GPa for intact cores and 17 GPa for a rock mass/22/. At 28 days, a modulus of 9 GPa has been obtained for a grout incorporating API Class H cement, fly ash, expansive additive, salt, water reducer, defoaming agent and water/6/. Another elastic property, Poisson's ratio, is approximately 0.18 for granite/22/ and 0.25 for cement-based

grouts/19/. The elastic and plastic properties of new sealants should be evaluated to ensure that a compatible system can be produced.

2.2.12 Radionuclide Retardation

It would be desireable for the sealant to retard radionuclides by sorption or other means of immobilization, thereby creating an additional barrier to ensure that the radionuclides cannot escape from the waste repository site/19,27/. Certain natural pozzolanic materials and mineral admixtures are capable of radionuclide sorption/28/ and the use of these materials will improve the plug's ability to retard radionuclides. However, due to other barriers, such as the backfill surrounding the waste package, this requirement is of secondary consideration.

2.3 Durability - Stability Requirements

To ensure the long-term performance of the plug-rock system, the stability of the plugging material with respect to the host rock, groundwater and environment is important.

2.3.1 Stability in Downhole Conditions

The sealant should be mineralogically stable under the pressure and temperature conditions present or expected in the borehole. These conditions can be simulated to ensure deterioration does not occur. The compressional wave velocity/18/, dynamic modulus/18/, and X-ray diffraction and scanning electron microscope photomicrographs/29/ can be compared at different ages to study long-term effects under extreme conditions on density, elastic modulus, mineralogy and morphology, respectively.

2.3.2 Chemical Stability

The host rock, plug and groundwater should be a chemically stable system. Reactions that will occur during the design life of the borehole plug must not cause detrimental changes to occur to the sealing ability of the plug. This will require a mineralogical and morphological determination of all materials by X-ray diffraction, scanning electron and optical microscopy/20/. Once these properties are determined, all thermodynamically possible reactions between the materials should be examined and the effect of these reactions on the plug's integrity evaluated/30/. Acceleration of reactions will require extreme care since: elevating temperatures may cause different reactions to occur; increasing the quantity of the reactants may alter the reaction; and ultrapulverization to encourage a reaction can cause phase changes/30/. Reactions will likely occur over the time span the borehole is to be sealed; therefore, these reactions must be analyzed to ensure that the plug continues to effectively seal the borehole.

2.3.3 Resistance to Groundwater Solutes

Resistance to sulphate, hydrogen, chloride and other aggressive ions is required for chemical stability/3/. This will require a prediction of the groundwater composition over the time span the borehole is required to be sealed. A variety

of sulphate resisting cements is available, while slag or fly ash additions have been found to be resistant to chloride solutions/31/.

2.3.4 Groundwater Leaching

A low leach rate is required to reduce the possibility of radionuclide movement and to reduce the detrimental changes that can occur to the sealant through leaching/19/. The leaching effects can be determined by inundating samples in simulated groundwater over long time periods and analyzing these samples for compositional changes and deterioration of physical properties.

2.3.5 Resistance to Natural Earth Currents

Stability to natural earth currents include stability to thermo-electric effects, telluric currents, oxidation potentials, electrokinetic or streaming potentials and contact potentials/32/. Electric fields may cause new minerals to form and therefore may cause adverse effects/32/. To reduce the effects of electrical currents, materials with low concentrations of sodium and potassium are required near the cathode/32/. In studying electric current effects, the groundwater composition should also be considered since electrochemical stability is also of importance/32/.

2.3.6 Resistance to Natural Geologic Processes

The bond strength, the compressive strength and other properties should be able to withstand the stresses created by long-term geologic processes and catastrophic processes. A nuclear waste repository should be located in an area of minimal seismic activity where movement of the entire storage system occurs under these processes, with no relative movement between components/32/.

Weathering is a natural geologic process also mentioned in the literature. The rate of weathering is required to be similar for the plug and host rock. The chemical composition of the precipitation (ie acid rain) will have an effect on weathering since mechanical erosion of granite is very slow unless the grains are loosened chemically/19/; therefore, this may require evaluation.

2.3.7 Long-Term Resistance to Biologic Attack

Geologic processes can be dependent on biologic agents. Anaerobic bacteria can produce reducing conditions, in turn causing the precipitation of metals from solution as sulphides. Biologic activities are very long-term processes, but the durability of the borehole plug can be adversely affected/32/.

2.3.8 Remarks

From the literature reviewed, these performance requirements have been mentioned as requiring evaluation. Not all requirements have numerical limits or defined methods of evaluation; therefore, these must be determined in order to properly evaluate the sealing materials. All the performance parameters outlined must be evaluated since it is unknown which will cause the failure of the borehole plug over the required design life of 10^4 to 10^6 years/33/.

3.0 MATERIALS FOR BOREHOLE PLUGGING

Most laboratories studying borehole sealing are studying the use of a cement grout as the plugging material or as a part of a composite plug. Other materials which have been considered for borehole sealing are presented in section 3.1 The use of cement based materials and additives is outlined in section 3.2.

3.1 Non-Cement Based Materials

Materials other than cement grouts which have been studied are presented in Table II. Of these materials, bentonite is actively being studied in Sweden as a plugging material/11/. A soil-bentonite backfill (gravel, bentonite pellets, shurgel (processed bentonite) and water) is recommended as part of a composite plug in basalt in the preconceptual work completed by Rockwell/34/.

The remainder of the materials listed are not being studied due to the questionable stability of organic materials, the shrinkage that results after placement and the problems associated with placement.

3.2 Cement Based Materials

The majority of research for borehole sealing at nuclear waste repository sites involves the study of cement grouts. Comments in some of the literature include, "cement appears to offer the best chance of achieving durable borehole seals using existing technology at an acceptable cost"/2/, and "the most advanced material currently available for plugging boreholes is high quality cement grout"/15/. The use of cements is also being studied since cements have a documented history of survival since, for example, 2000 year old pozzolanic cements still perform well in surviving Roman structures/5*/. As well, the major cement hydrates, for example tobermorite, can be found as naturally occurring minerals, indicative of their geologic stability/55/. They also exhibit low permeability, high adaptability, a low cost and are readily available/33/. The resistance to leaching, thermal stability, conductivity and radiation stability are other reasons for the consideration of cement based materials as borehole sealants/27/.

3.2.1 Types of Cements

The use of oil-well cements and portland cements for plugging boreholes is presently receiving the greatest attention in experimental research. A comparison of the oxides of cements to the formational rock granite indicates that a compatible system can be obtained (Appendix A). Cements with mineral and organic additives have the potential of producing a plug with the desired properties described previously.

Presently, most grouts being studied are sulphate resistant cements with fly ash added to improve permeability and chemical stability. To achieve expansion and

*Since the time of this review several references on ancient concrete have been published/56,58,59/.

also to allow the use of low water-cement ratios, special cements are used as well as additives. In Table III, an outline of grouts which have been studied at different laboratories is presented. An indication of the alternatives available and the wide variety of materials being studied can be obtained from the table.

From the literature, comparisons of candidate materials have shown that:

(a) In comparing permeabilities of fly ash, sand and water mixes with API Class H, Class C and ASTM Type I cements, the lowest permeabilities were obtained with Class H cements/13/.

(b) All particles of Class H cement are 100 microns or less in diameter as compared to Class C cement which has particles of 70 microns or less/4/. This may be a concern with respect to sealing small fissures around the borehole plug where finer grain grouts would be advantageous.

(c) Cements, especially Class G and Class H cements, have very low sodium and potassium contents/19/; therefore, long-term stability with respect to natural earth currents should be more easily obtained with Class G and Class H cements.

3.2.2 Mineral and Liquid Additives

A variety of additives has been incorporated into cement grouts for borehole sealing. They are presented in Table IV with comments on their effectiveness in achieving the performance requirements. The mineral additives outlined include fly ash, natural pozzolans, aluminum powder, silica powder, and bentonite. Liquid additives include dispersants, defoamers, superplasticizers/water reducing agents and set retarders.

4.0 DISCUSSION

The possibility exists that no boreholes requiring sealing will be present in a repository since the exploratory boreholes can be drilled at the locations of future shafts/35/. It is considered by some researchers that boreholes are but minor pathways for the escape of radionuclides to the biosphere and therefore may not require extreme care in sealing/36/. These comments imply that borehole sealing may not be critical in the total scheme for nuclear waste repository sealing, but these views are controversial and research must continue to produce the best borehole sealing method possible. An effective method for sealing boreholes is required in order to receive public acceptance of nuclear waste repositories and to ensure that a method is available if additional boreholes are required during the construction of the repository.

Repository sealing will not occur until well into the 21st Century. Therefore, the need for borehole sealing materials and methods is not immediate. However, research on new and less well known alternatives should be considered since these may prove in the long run to be of a far superior quality to any of the

sealing materials presently known/37/. Research requiring long-term monitoring should also be continued over the available time span since the long-term integrity of the borehole sealing materials is of great importance.

An evaluation of materials at this time is quite difficult. In assessing cement grouts, for example, the experimental work in many cases has been limited to grouts incorporating several different additives. This causes difficulty when it is required to determine the additive that resulted in a particular effect. Difficulties also arise since the experimental results reported at different laboratories cannot be directly compared due to differing experimental procedures and due to the use of different additives. Therefore, even though a great deal of work has been completed on borehole sealing materials, much more research is required to produce a plugging material capable of optimizing all the performance requirements outlined previously.

5.0 RECOMMENDATIONS

The following recommendations deal mostly with cement based materials since little work has been done on other materials:

(a) An attempt should be made to evaluate and determine the limits for all the performance requirements in order to develop a method of selecting the optimum sealing material. If limits cannot be determined, then properties should be compared to those of an arbitrary reference sealing material. This aspect of the borehole sealing program should be addressed at the earliest possible date.

(b) A general consensus exists among researchers that the selection of a plugging material must be site specific, considering the local hydrologic, geochemical and other environmental factors/38/. For this reason, information should be obtained at the earliest possible date on the host rock, groundwater and precipitation expected at the waste repository site.

(c) Cement grouts should be studied for borehole plugging since research completed to this time has indicated a reliable plug can be developed using cement grouts. CSA Types 30 and 50, as well as API Class C and Class H cements have been studied elsewhere; therefore, it may prove useful to employ some or all of these cements as reference cements in further study.

(d) It is recommended that studies be undertaken which address the feasibility of using cement grouts to seal small fissures. This will require the development of procedures that enable the determination of the size of fissures that can be filled. Once the size of fissures that can be sealed is determined, a secondary material may be required to be studied to seal smaller fissures.

(e) Supplementary cementing materials such as fly ashes, blast furnace slag and silica fume should be studied since they offer the potential for improved physical properties and durability. With respect to fly ashes, low lime fly ashes (ASTM Class F) are recommended over high lime fly ashes since lower permeabilities and better chemical resistance are obtained using this

type of fly ash. The compressive strength is sufficient and a low lime fly ash has the best potential to match the oxide composition of the host rock.

(f) A study of volumetric stability should be undertaken that includes evaluation of the volume change, permeability (of the grout as well as the grout/rock interface) and bond strength. If, on the completion of testing, the quality of the sealant is shown to be inadequate, then expansive cement systems should be studied. It should be noted that most researchers studying cement grouts for borehole sealing include expansive additives.

(g) If the use of natural earth materials is to be pursued as an alternate plugging material or as a part of a composite plug, the development of downhole compaction equipment is required along with assurance of erosion resistance.

(h) Accelerated testing methods should be developed and evaluated to reproduce the reactions likely to occur during the design life of the borehole plug.

These are general recommendations for the borehole sealing program. The next stage would be to develop specific test procedures and programs for further study in consultation with other members of the larger borehole and shaft sealing program within the Civil Research Department.

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TABLE I

Performance Requirements

A. PLACEMENT REQUIREMENTS	B. MECHANICAL PROPERTY REQUIREMENTS	C. DURABILITY-STABILITY REQUIREMENTS
1. Working Time	1. Permeability	1. Stability in Downhole Condition
2. Bleeding and Segregation	2. Porosity	2. Chemical Stability
3. Fluidity	3. Density	3. Resistance to Groundwater Solutes
4. Pumpability	4. Strength	4. Groundwater Leaching
5. Sealing of Fissures	5. Bond Strength	5. Resistance to Natural Earth Currents
	6. Expansion	6. Resistance to Natural Geologic Processes
	7. Homogeneity	7. Ability to Withstand Weathering
	8. Moisture and Thermally Induced Shrinkage	8. Long-term Resistance to Biologic Attack
	9. Deformability	
	10. Thermal Properties	
	11. Elastic and Plastic Properties	
	12. Radionuclide Retardation	

TABLE II

Borehole Sealing Materials

Material	Description and Comments	
	Advantages	Disadvantages
Compacted Earth Materials	- long-term durability possible	- downhole compaction equipment not yet developed/39/ - contamination possible from fluids present in the borehole/39/ - instrumentation required to assure quality control of compaction process/39/ - the use of actual formation materials produce plugs with no bond (less than 10 psi) have little compressive strength and a higher permeability than surrounding rock/40/
Melting of Formational Materials/40/	- considered in salt formations	- contracts on cooling - cracking results
Polyester Sealants/40/	- high compressive and tensile strength	- difficult to mix and control setting time - most use a peroxide catalyst which is highly flammable - mishandling can cause separation or dry out to occur and material can become shock sensitive
Asphalt and Gilsonite/40/	- durability of 3000 years known, used by Babylonians	- melting required for placement - greater than 1% linear shrinkage occurs on cooling

TABLE II (cont'd)

Material	Description and Comments	
	Advantages	Disadvantages
Basolit 600/40/	- a sulphur based inorganic sealant	- required to be at 250°C to be poured - when cooled to 75°C, 1% shrinkage occurs
Nukem 200/40/	- inorganic sealant	- shrinks on cooling - water soluble
Silica Gel		- acid conditions of groundwater can affect gel properties/39/
Silicone Rubber/40/		- placement is difficult, high viscosity - shrinkage results
Phenol Formaldehyde and Phenol Furfural Resins/40/		- stability is questionable - water is released during setting resulting in 0.5% shrinkage
Epoxy Cement and Resin	- an organic material/40/ - high compressive and very high bond strength/39/	- bond lost in 45 years in the presence of moisture, if bonded to smooth glass (formational deformation may allow maintenance of a good bond)/40/ - questionable stability over 100's of years

TABLE II (cont'd)

Material	Description and Comments	
	Advantages	Disadvantages
Plaster of Paris/40/		- unstable at elevated temperatures - less strength than Portland Cement - high permeability as compared to Portland Cement - less permanency than Portland Cements
Gypsum		- converts to Plaster of Paris/40/
Polymer Cements/39/	- high strength - low permeability - very durable - less batch-to-batch variation	- have not been found to be durable at high temperatures (300°C) - more costly than inorganic cements - long term durability questionable, since it is an organic
Amber	- natural organic material/33/ - translucent fossil resin/41/	- since organic, questionable stability/41/
Aluminous Cements		- crystal change occurs at temperatures above 27°C, resulting in a temporary loss in strength/40/

TABLE II (cont'd)

Material	Description and Comments	
	Advantages	Disadvantages
Bentonite	- clay rich in montmorillionite/42/ - has the ability to swell, absorb and exchange ions	
	- chemically stable at temperatures lower than 100°C/43/ - chemically stable for the pH values found in granite in Sweden/43/ - lab permeabilities of 10^{-12} to 10^{-13} m/s/44/ - swelling produces tight contact with walls and eliminates leakage	- chemical stability is affected by changes in pH and temperature/44/ - ion exchange can occur to sodium bentonite if in the presence of calcium ions resulting in an increase in permeability/44/ - erosion may result when under high water head in unconfined conditions
Hydrothermal Cements	- mixtures of poorly crystalline calcium silicate hydrate, tobermorite or a solid solution of this phase and a residue of quartz/39/	
	- from engineering and economic standpoint hydrothermal cements are the most feasible of all materials placed by hydrothermal transport/39/ - can seal as effectively as a low temperature cement grout/39/ - permeabilities improve as recrystallization takes place/39/ - higher long range thermodynamic stability as compared to low temperature cement grouts/45/	- placement may be feasible but technological difficulties do exist/39/ - initial permeability higher than low temperature cement grout/39/ - high temperatures and pressures increase rate of reaction, rock-grout interactions have a greater potential of occurring/39/ - at planned repository depths of 1 km, rock masses will be cool and hydrothermal pumping will likely be inadequate to have any beneficial effect

TABLE III

Cements and Additives Studied for
Expansion and Low-Water Demand

Laboratory	Type of Cement	Expansion	Low-Water Demand
Rockwell International Laboratory/5/	Portland Type V	Aluminum Powder	Plastiment (organic water reducing agent and set retarder)
Sandia Laboratories/9/	Class H	Expansive Additive	Class H cement
Sandia Laboratories/1/	Type E-1 (K) expansive cement (ASTM designation)	Type E-1 (K) expansive cement	Melment M-10 (water reducer) Plastiment
Oak Ridge National Laboratory/46/	Class H	Expander A	Class H cement Plasticizer D-65
Penn State* University /6/	Class H	Expansive Additive	Class H cement Superplasticizer, melamine formaldehyde condensate

*Note: This mixture was used in a study completed by Penn State and the US Army Engineers Waterways Experiment Station to determine if similar experimental results can be obtained using similar materials in two different labs.

Note: Other additives are also present in the grouts being studied. This table considers those imparting expansion and low-water demand properties.

TABLE IV

Grout Additives

Additive	Laboratory	Description and Comments	
		Advantages	Disadvantages
Fly Ash		- an excellent pozzolan/17/ - reduced early age strength/8/ - contributes to later age strength and durability/9/ - no effect on density of grout/17/ - no significant effect on thermal conductivity/17/ - no significant effect on shrinkage/17/ - increased resistance to sulphates/49/	- generally improves resistance to sulphate but this must be confirmed for any particular fly ash
- low lime fly ash	Oak Ridge	- lower ultimate permeability than ashes with high lime contents - greatest potential for chemical stability in granite (Appendix A) - long term durability of pozzolanic cements (in most cases low lime) imply potential of long-term durability/5/	- lower early compressive strength than ash with higher lime content/4/ - high-carbon fly ash had higher water demand than low-carbon fly ash/48/
- high lime fly ash	Sandia	- higher compressive strength than low lime fly ash grouts/4/	- permeability increases with increasing lime content in fly ash/13/
		Note: Largest compressive strengths produced with lime content of 15%, compressive strength decreases for fly ash of 25% and decreases to a lower strength for fly ash of 1.3% lime content/4/.	

TABLE IV (cont'd)

Additive	Laboratory	Description and Comments	
		Advantages	Disadvantages
Natural Pozzolan	Rockwell	- natural high silica-pozzolan/5/ - Roman work of 2000 year age used pozzolanic cements/5/ - reduced bleeding and segregation/5/ - lower heat of hydration/5/ - lower thermal shrinkage/5/ - improved long-term integrity and durability/5/ - most have low lime content/49/ - reduced shrinkage/5/ - increased workability/33/ - improved permeability/5/ - improved stability of cement mixtures exposedto moderate temperatures/5/	- higher cost as compared to fly ash
Dispersant	Sandia	- napthalene condensate dispersant causes a reduction in the apparent slurry viscosity/50/	
Defoamer	Sandia Oak Ridge	- required in high density slurries to obtain appropriate densities/9/ - reduces amount of air entrapped/9/	

TABLE IV (cont'd)

Additive	Laboratory	Description and Comments	
		Advantages	Disadvantages
Latex		- most have particle size of less than 20 μm - increased compressive and tensile strength - improved deformability - decreased void/cement ratio - increased modulus of rupture	- long term stability of organic materials not known
		Note: Since not from borehole sealing literature, testing of shrinkage, permeability, not completed.	
Aluminum Powder		- causes expansion of plastic grout by formation of gas bubbles	- good quality control required/49/ - placement of mortar should take place within 45 minutes of mixing/49/
- unpolished (commercial grade)	Rockwell		- shrinkage is observed to occur/5/ - increase in water/cement ratio required to achieve same workability/5/ - segregation and bleed increases/5/ - density decreases/5/ - set of mixture accelerates/5/

TABLE IV (cont'd)

Additive	Laboratory	Description and Comments	
		Advantages	Disadvantages
Aluminum Powder			
- polished	Rockwell	- expansion produced/5/ - improves contact with irregular surfaces/5/ - plastic shrinkage counteracted/39/ - 15-20% water content produces some flowability/39/ - fluidity or flowability increased by 300%/39/ - bleed and segregation reduced/39/ - frost resistance improved/39/	- results in lower density, higher porosity concrete - setting and 'free-flow' time is extended/39/
Silica Powder	Rockwell	- reduces deterioration at elevated temperatures/45/ - a denser, stronger final product produced (tobermorite)/45/ - decreases permeability/50/ - increases ultimate compressive strength/50/	
Silica Powder or Flour		- reduced shrinkage/5/ - improved thermal stability/5/	

Note: Temperatures greater than 100°C are not expected to occur in the borehole.

Recommended for use in basalt formations where temperatures are greater than 100°C/5/.

TABLE IV (cont'd)

Additive	Laboratory	Description and Comments	
		Advantages	Disadvantages
Superplasticizers/18/ or water reducing agent	Rockwell (Plastiment) US Army Engineer WES (Melment L-10) Oak Ridge	- increases density - water required for same workability is reduced	- most are organic, effect on long-term stability unknown
Expansive Additives /9/	Sandia Oak Ridge	- reduces permeability at plug-rock interface - compensates for shrinkage of concrete - improves bond between plugging material and formational rock - no effect on density or permeability	- some are organic
Bentonite /39/		- up to 8% is commonly used - sedimentation of cement particles is retarded - reduces bleeding	- reduces strength
Silica Sand/51/	Sandia	- improves strength characteristics - reduces circulation loss to the formation	
Set Retarding Admixtures/52/	US Army Engineer WES (Plastiment)	- 2 hour setting time without admixture - 4 hour setting time with 3% admixture (melamine) - 5 hour setting time with 2% admixture (naphthalene)	

Other materials used as additive include aggregates, bentonite gel and salt (in areas of salt formations).

APPENDIX A

Chemical Compatibility Between Host Rock and Plug

The long-term stabilities of cement grouts are feasible since granite and cements share many of the same oxides/53/. Table A-1 gives a listing of these compositions along with a typical low and high lime fly ash. In oil-well cementing practice, a 43 to 34 ratio of cement to fly ash is used/19/. To give a comparison of granite to grout, this ratio will be used for the four combinations. These are given in Table A-2.

The actual granite composition may yield different values since this is a very general composition. Due to the low lime content of the granite, a fly ash with a lower lime content would produce a grout that most closely resembles the composition of the granite. Variations exist in the compositions, but varying the cement-fly ash ratio and the use of additives may produce a grout that is chemically stable.

Consideration of oxide composition indicates that a low lime fly ash would produce a grout with a greater possibility of stability.

Comparing oxide contents is a simple method used by Gyenge to evaluate stability/19/. The minerals of the host rock and the plug material should actually be compared since it is known that the minerals formed depend on the temperature and pressure to which the grout will be subjected. The minerals that form for different cements and temperatures are presented in Figure A-1. To evaluate chemical stability a study of the mineral composition of the grout under the conditions expected in the borehole during setting and the possible changes that can occur to the mineral composition under the expected pressures and temperatures during the life of the plug should be determined and compared to the mineral composition of the host rock.

TABLE A-1

Percent Oxide Compositions of
Granite, Cement and Fly Ash

Oxide	Granite /54/	API Class G or H Cement/19/	ASTM Type V Cement /4/	P-15 ASTM Class F Fly Ash/4/	P-8 ASTM Class C Fly Ash/4/
SiO_2	52	22.45	22.7	48.6	39.7
Al_2O_3	14.5	4.76	2.99	29.5	19.4
Fe_2O_3 FeO	)))))	4.10	2.90	9.0	5.40
CaO	9	64.77	65.68	1.3	24.78
MgO	6.5	1.14	1.63	1.3	3.95
Na_2O	2	-	0.24	0.3	1.64
K_2O	0.5	0.08	0.38	3.1	0.48
SO_3	-	1.67	1.90	0.4	0.27
Loss on Ignition	-	0.54	0.42	2.8	0.81
P_2O_5	-	-	0.14	1.0	1.85
C	-	-	-	2.7	0.84
TiO_2	-	-	0.23	-	-

TABLE A-2

Grout and Granite Percent Compositions

Oxide	Granite/54/	Class G or H Cement + P-15 Flyash	Class G or H Cement + P-8 Flyash	Type V + P-15 Flyash	Type V + P-8 Flyash
SiO_2	52	34.00	30.07	34.14	30.21
Al_2O_3	14.5	15.24	11.22	14.25	10.24
Fe_2O_3 FeO	)11	6.26	4.67	5.59	4.00
CaO	9	36.74	47.11	37.25	47.62
MgO	6.5	1.21	2.38	1.48	2.65
Na_2O	2	0.13	0.72	0.27	0.86
K_2O	0.5	1.41	0.26	1.58	0.42
SO_3	-	1.11	1.05	1.24	1.18
Loss on Ignition	-	1.54	0.66	1.47	0.59
P_2O_5	-	0.44	0.82	0.52	0.90
C	-	1.19	0.37	1.19	0.37
TiO_2	-	-	-	0.13	0.13

FIGURE A-1

Effect of Temperature and Calcium to Silica Ratio on Mineralogical Compositions of Calcium Silicate Hydrates/55/

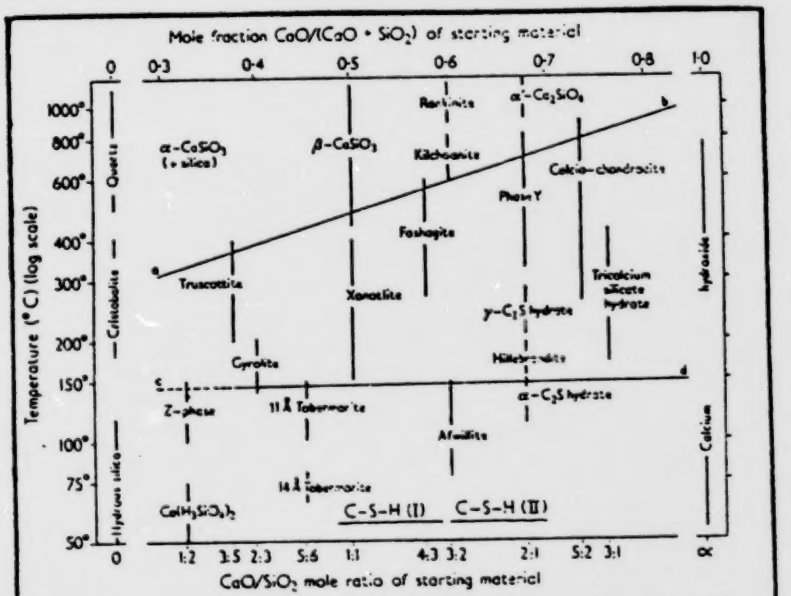

FIG. 15. Diagram showing the approximate conditions of formation of the better established anhydrous and hydrated calcium silicates under hydrothermal conditions. Vertical lines indicate Ca/Si mole ratios of compounds. The extension of each line gives an indication of the range of temperature over which the compound is formed, while displacement of the name to either side of this line indicates that the compound tends to form not only from mixtures of its own Ca/Si ratio, but also from mixtures of higher or lower Ca/Si ratio. Wavy underlining denotes variable composition. For temperatures up to 374°C, saturated steam pressure is assumed, and for higher temperature the water pressure is assumed to be around 400kg/cm². For significance of lines ab and cd, see text.